

CHEMICAL AND BIOLOGICAL BARRIER MATERIALS FOR COLLECTIVE PROTECTION SHELTERS

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ABSTRACT

Collective Protection Shelters have historically been heavy, cumbersome, carried a high logistic burden, and above all been very expensive. Through the years several advances have been made in barrier materials to improve the protective capabilities of collective protection shelters. These barrier materials generally fall into several categories including butyl rubbers, chlorinated aliphatics, and fluorinated polymers. The degree of protection these barrier materials provide against the permeation of a "challenge agent" is often overshadowed by several factors including thermal stability, flame resistance, ease of decontamination, longevity of the material, leakage points due to closures/seams and cost. However, when human lives are at stake the most important factor is the degree of protection the material provides against permeation of a chemical or biological threat. Unfortunately, the exact nature of the threat is often unknown and a particular material may vary in protective properties from one challenge to another. The focus of this paper is to give a brief history of the U.S. Army's chemical and biological barrier material program, for collective protection, as well as the current and future thrust areas of research and development.

BACKGROUND

The U.S. military fielded the first Collective Protection systems in the 1960's. This system consisted of a soft-wall shelter and an environmental control system, which included a filter and blower unit to clean contaminated air as well as overpressure the shelter. The first transportable Collective Protection system, M51 (See Figure 1), was approximately 300 square feet in size and was mounted on a one-and-a-half-ton trailer. The M51 used a neoprene coated Decron® substrate with a Tedlar® film laminated on the surface to serve as the chemical and biological barrier. This material allowed the shelter to conduct medical operations in a chemical, biological and nuclear contaminated environment. Although relatively effective as a barrier, withstanding agent challenges of 100 minutes for Mustard (HD) and 200 minutes for GB (Sarin), the shelter was logically burdensome weighing 5700 lbs, taking 5 persons 30 minutes to strike. Furthermore, a generator was needed to run constantly to maintain pressure in the Airbeam support structure.

The Tedlar®/Decron® material possessed many flaws, which only added to the logistical burden of fielding the shelter. These flaws included: high expense as compared to conventional general-purpose material; difficult to heat weld or adhesively bond material during manufacturing; residual creasing after storage or repeated deployment; very heavy and cumbersome to deploy; and the Tedlar® barrier was subject to flex cracking, especially in cold weather. The composite material could be decontaminated if the barrier film was placed on the outside of the shelter, however this would subject the barrier film to abrasion. The ultimate showstopper for the M51 was the need for a dedicated vehicle. Since the system was on a trailer the vehicle would frequently be used for other duties and would not be available when required.

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Figure 1. M51 Chemical and Biological Protective Shelter.

Since the 1960's advances in materials and processing techniques allowed for material composites to be better optimized for specific uses such as collective protection shelters. Prototype shelters provided an ideal forum to investigate new barrier materials for experimental development. In the 1980's alternatives for an outer CB skin material were investigated. Initially, five composite materials were identified as possible replacement candidates for the M51 barrier material. These candidate materials consisted of butyl nylons, Teflon®/Kevlar®, Tedlar®/vinyl coated Dacron®, Teflon®/Nomex®, and polyester/Tedlar®/Kevlar®. Since Tedlar®/vinyl could not be purchased in weights less than 20oz/yd² it was eliminated during the initial down selection. Teflon®/Nomex® was also eliminated initially because it was similar to the Teflon®/Kevlar® yet lacked the physical characteristics of the Teflon®/Kevlar® composite. The remaining three candidate barrier materials were further investigated by conducting physical and chemical testing.

Characteristics that were investigated included CB resistance, flammability, weight, flexibility, durability, manufacturing characteristics, material costs and decontamination characteristics. Upon completion of testing, the material with the most potential was found to be the Teflon®/Kevlar® composite. The Teflon®/Kevlar® material was chosen based on its superior CB resistance, ability to be decontaminated, weight, mechanical properties, and the ability to heat-seal during fabrication. Unfortunately, the high temperatures needed to heat-seal Teflon® drove up manufacturing costs while the use of Kevlar®, required to produce a lightweight substrate as well as survive the high temperatures during welding, drove up the material costs. The end item became a very expensive solution, but when human lives were at stake it became the most viable prototype material.

The Teflon®/Kevlar® material was used in several shelters before ultimately ending up in the Chemical and Biological Protective Shelter System (CBPSS) (See Figure 2). The CBPSS overcame the major shortcomings of the M51 by improving the barrier material as well as providing a dedicated HMMWV. This HMMWV was augmented with a hydraulic driven environmental control unit to provide heating and cooling, as well as a filtered air supply which also provided overpressure to the shelter.



Figure 2. Chemical and Biological Protective Shelter System (CBPSS).

In addition to an outer barrier material for collective protection, an internal liner material was developed to provide collective protection to existing general-purpose shelters. The liner was originally developed in the 1970's for the Secret Service. This system, the M20, provided chemical and biological protection for buildings. The system was later modified in the 1980's to fit inside the Tent Extendable Modular Personnel tent (TEMPER) for primarily medical operations and renamed the M28 (See Figure 3). The M28 utilized an over-pressured polyethylene (HDPE/LDPE) material with a poly-vinylidene chloride (PVDC) internal barrier layer. This liner provided a relatively inexpensive means of providing chemical and biological protection for general-purpose shelters. The drawback of this liner, as compared to an outer shell fabric, includes increased packed volume/weight and double the deployment time since these liners are integrated with the support system of the shelter. Another major issue with the liner is the severe limitation it places on mission flexibility, since the liner could neither be installed after the original deployment, nor removed mid-mission. Currently fielded liners have flame and UV issues as well but solutions have been identified and are presently being investigated through the Joint Collective Protective Equipment program (JCPE). The M28 liner material has been utilized by the joint services in varying configurations such as the Army Chemical Protection Medical System (CP DEPMEDS), the Marine Corps Portable Collective Protection System (PCPS) and the Air Force Chemically Hardened Air Transportable Hospital (CHATH)



Figure 3. M28 liner: PVDC internal barrier with a HDPE scrim and a LDPE protective coating.

In conclusion, currently the U.S military has only two viable options for chemical and biological protective materials. These options are either the expensive, high-performance, decontaminable material (Tedlar®/Kevlar®) or a lightweight, low cost liner material, which has minimal physical properties, absorbs agent, is non-decontaminable, and carries the logistical burden of shipping, storage, and deployment (M28 liner material).

TECHNOLOGY DEVELOPMENT

Over the past several years, the Joint Science and Technology Panel for Chemical and Biological Defense (JSTPCBD) has funded research to investigate and develop the next generation barrier materials for collective protection shelters. The goal has been to develop a lightweight material with improved UV and flame resistance, increase durability, improved permeation properties and decreased cost from a material as well as a manufacturing standpoint, as compared to currently fielded materials.

To mitigate risk and provide incremental improvements to existing chemical and biological protective barrier fabrics, near-term, mid-term and long-term solutions have been identified and are currently being investigated. These solutions are constantly being revised as new technologies emerge and existing technologies overcome technical barriers. To date, the thrust of the research has been focused on fluoropolymer coatings as an after-market process for general-purpose shelter materials, nanotechnological enhancement of commodity polymers, low temperature processible fluoropolymers and self-decontaminating barrier materials incorporating catalytically reactive membranes. Each of these thrust areas have their own technical challenges and associated investments to mature the technologies.

Due to limited options for a chemical and biological protective barrier material and the growing threat of CB warfare, in conjunction with lessons learned from the Gulf War, a technological development effort was initiated in 1998. This effort began with the investigation of commercial fabrics, polymers, coatings and laminates that have inherently good chemical and biological resistance. Fluorinated polymers offer exceptional permeation properties but are traditionally difficult to process and therefore costly. In contrast, chlorinated polymers are relatively cheap to process, however absorb agents and disintegrate with exposure to current decontamination fluids. Conceived from this initial investigation

three thrust areas were identified as viable approaches to our near and mid-term solutions. These approaches included: applying a CB barrier film/laminate to general-purpose fabric, which has a proven history of durability and is cost efficient throughout its life-cycle; improving the existing polyethylene liner material which is a lightweight, low cost solution, and examining the building blocks of conventional fabrics and polymers to produce a high strength to weight ratio substrate with a thin fluoropolymer film which will provide the composite fabric with chemical and biological resistance.

Near-Term Solution

The near-term solution has been focused on improving barrier properties through coating general-purpose fabrics currently used in shelters. This approach has the lowest technical risk and is cost effective for providing improved chemical and biological protection for existing general-purpose shelters. The key advantage of this approach is providing a dramatic improvement in chemical and biological resistance to standard tent fabric with a minimal increase in weight.

The standard tent fabric is a woven polyester fiber with a polyvinyl chloride (PVC) coating. This coating serves as both a repellent to liquids as well as a means of heat-sealing the fabric thus increasing the efficiency of manufacturing. A major laminating house, Duracote Corporation, Ravenna, Ohio, was contracted to laminate various low temperature fluoropolymer films of varying thickness to both one side and two sides of the fabric. Permeation testing was then conducted and initial results proved very promising.

A volatile organic simulant, tetrachloroethane (TCE), is initially used to screen out candidate materials. It is a relatively cheap agent to use before more extensive/expensive simulant testing is conducted. This simulant is not intended to simulate a CB agent but rather to test the relative permeation of a material based on known permeation values through 'good' barrier materials.

The control fabric, standard PVC/polyester, typically reaches an equilibrium flux of 17,000 g/dm². Several candidate composites were fabricated by Duracote and tested using TCE (See Figure 4). Results of the initial testing showed a significant reduction in equilibrium flux especially in samples #5 & #8, which showed very little permeation after 120 minutes.

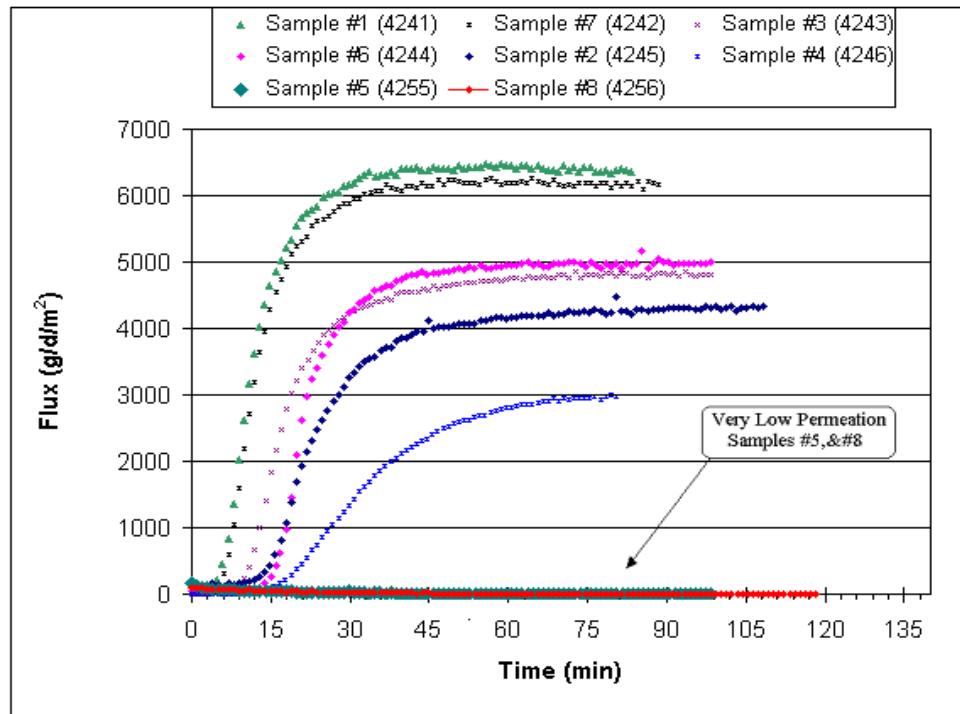


Figure 4. Tetrachloroethane (TCE) Permeation Through Duracote Samples.

The best candidate fabrics from the permeation testing (#5 & #8) were then subjected to physical testing according to MIL-C-44103C. This was to insure the coatings didn't have any negative effects on the composite material such as flame, IR signature, or interference with the ability to heat/RF weld the fabric using conventional welding equipment. Initial test results were very positive and a limited production quantity of the new CB enhanced polyester/PVC fabric was ordered. The material was to be used to build a prototype shelter and to conduct operation testing. Unfortunately, the material hit a technical barrier with problematic delamination/streaking issues. Currently the U.S. Army is attempting to overcome this technical barrier to provide a transitional near-term solution.

Mid-Term Solution

The mid-term solution includes nanotechnological enhancement of commodity polymers and lower temperature processible fluoropolymers. Both of the mid-term approaches have shown much promise and should be transitioned within the next 2-4 years.

Nanocomposite Liner Material

Through the introduction of nanoscale particles into commodity polymers, improved barrier properties can be achieved. This technology has been proven and applied in industries ranging from food packaging to pharmaceuticals to consumer goods. Triton Systems, Inc. of Chelmsford, Massachusetts, has extensive experience in the subject area of nanocomposites. They have successfully demonstrated the improvement in barrier properties for materials such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), melt processible rubber (MPR), thermoplastic polyurethane (TPU) and several other proprietary polymers. Through the introduction of nano-clay platelets at between 5% and 10% by weight, barrier properties have increased between 30% and 200% for a 10-20 mil thick film. This increase in barrier properties is also done without significantly changing the physical properties of neat polymers. In fact, these nano-clay platelets have shown an improvement in flame and ultraviolet resistance for the composite.

Triton Systems, Inc. was contracted by the U.S Army to improve the barrier properties of the M28 liner material as well as improve flame and UV resistance. The polyvinylidene chloride (PVDC) barrier, as mentioned above, is a proven protective barrier. However, improving the flexibility of the barrier film and adding the capability to seal the material with radio frequency equipment could achieve a lower cost of production and manufacturing. Triton Systems Inc. has investigated several proprietary barrier films and has demonstrated the improvement of the existing PVDC barrier properties through application of their nanocomposite technology.

Initial testing using TCE showed a significant improvement in barrier properties through the application of nanocomposite platelets. As shown in Figure 5, permeation values for all controls samples, materials currently used in the M28 liner, were significantly improved. Of considerable interest were the results of a proprietary nano barrier film, which showed zero permeation after 640 minutes of testing.

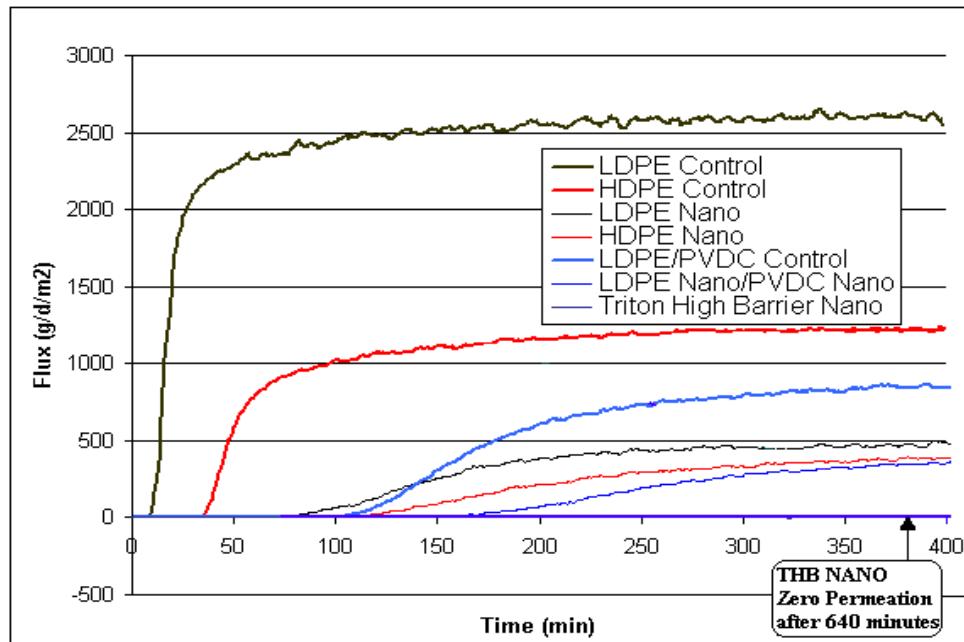


Figure 5. Tetrachloroethane (TCE) Permeation Through Nanocomposite Samples.

Live agent testing was also conducted on Triton's high barrier nano film, which showed excellent resistance. (See Figure 6) The nano film showed no permeation of liquid mustard (HD) after 24 hours and no permeation of Sarin (GB) after 72 hours. This matches or exceeds currently used barrier films under similar conditions.

Sampling Intervals (Hours from Start) ($\mu\text{g}/\text{cm}^2$)										
Agent	Sample	(0-2)	(2-4)	(4-6)	(6-8)	(8-12)	(12-24)	(24-48)	(48-72)	Cumulative
HD	Neat	ND	ND	ND	ND	ND	ND	0.1	0.15	0.25
	TSI Barrier Film	ND	ND	ND	ND	ND	ND	ND	0.2	0.2
GB	Neat	ND	ND	ND	ND	ND	0.00016	0.00036	0.00037	.00089
	TSI Barrier Film	ND	ND	ND	ND	ND	ND	ND	ND	ND

Figure 6. Live agent testing on Triton High Barrier Nano film.

Triton Systems, Inc. is currently working on scaling up their technology to produce enough material to laminate a high barrier film to a woven HDPE scrim to produce a non-decontaminable CB resistant tent liner similar to the M28. They will also laminate a high barrier film to a high strength fabric substrate to produce a decontaminable outer skin fabric. These materials will then be tested and evaluated for physical as well as chemical and biological properties.

Low-Temperature Processible Fluoropolymers

The use of aramids such as Kevlar provides an extremely strong and inherently flame resistance substrate. This substrate can also withstand the high temperatures necessary to bond conventional

fluoropolymers such as Teflon[®] to provide a chemical and biological barrier for the composite material. Unfortunately, aramids such as Kevlar[®] are not only expensive but provide more strength per denier than needed for the application. The availability of a low temperature processible fluoropolymer that would provide comparable barrier properties comparable to Teflon[®] would allow the use of a low cost substrate, which would not need to resist such high temperatures.

An investigation of commercially available fluoropolymers as well as chloropolymers of varying compositions was conducted. The goal was to find a low temperature processible polymer with improved durability, ease of processing, or improved resistance to chemical and biological agents over the existing Teflon. Once a candidate barrier material was identified a compatible substrate material needed to be found. The final composite also needed to have the physical properties of a general-purpose fabric, which meets MIL-C-44103C requirements, as well as resist permeation of conventional threat agents for 72 hours with no measured detection.

Federal Fabrics-Fibers Inc. (FFF), of Lowell, Massachusetts, has an extensive knowledge base of high-tech fibers and textile manufacturing processes. FFF is currently funded to produce a void free lightweight fabric substrate with a chemical and biological barrier. They use a building-block approach, first producing coated yarns, weaving and lastly coating to produce a fabric that is void-free, heat-weldable, decontaminable and chemical and biological resistant. They have successfully demonstrated the ability to produce a low cost, lightweight, CB resistant, decontaminable fabric. FFF has scaled up their facilities and should have production capabilities in place by the end of this year. They have identified a low temperature fluoropolymer, which is easily processed with conventional equipment and can readily be heat welded. The fluoropolymer laminate is also very resistant to conventional decontamination solutions.

Initial testing of FFF's proprietary low-temperature processible fluoropolymer has shown very promising results. The film has shown very little permeation of TCE during initial simulant testing conducted over a year ago. (See Figure 7)

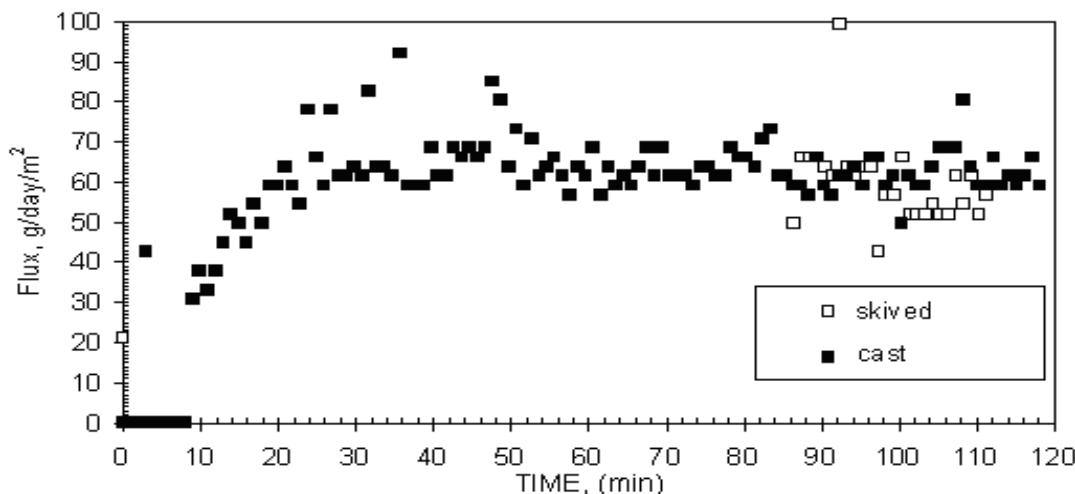


Figure 7. TCE Vapor Flux through Fluoropolymer Samples.

The film has also been tested for decontaminability showing very little mechanical degradation when subjected to Super Topical Bleach (STB) and Decontamination Solution Two (DS2) (See Figure 8 & 9).

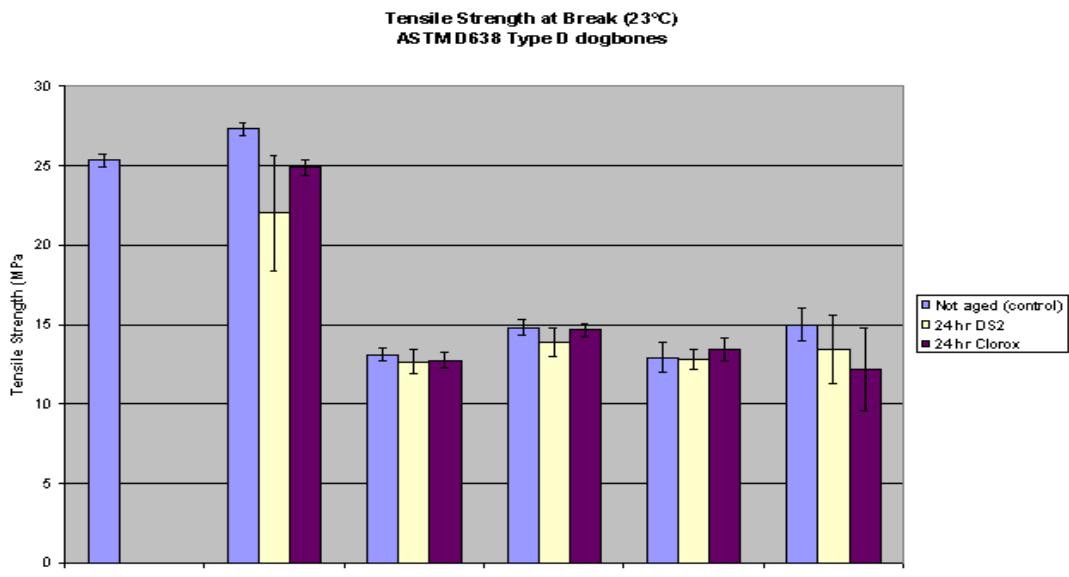


Figure 8. Effects on tensile strength using various decontamination solutions.

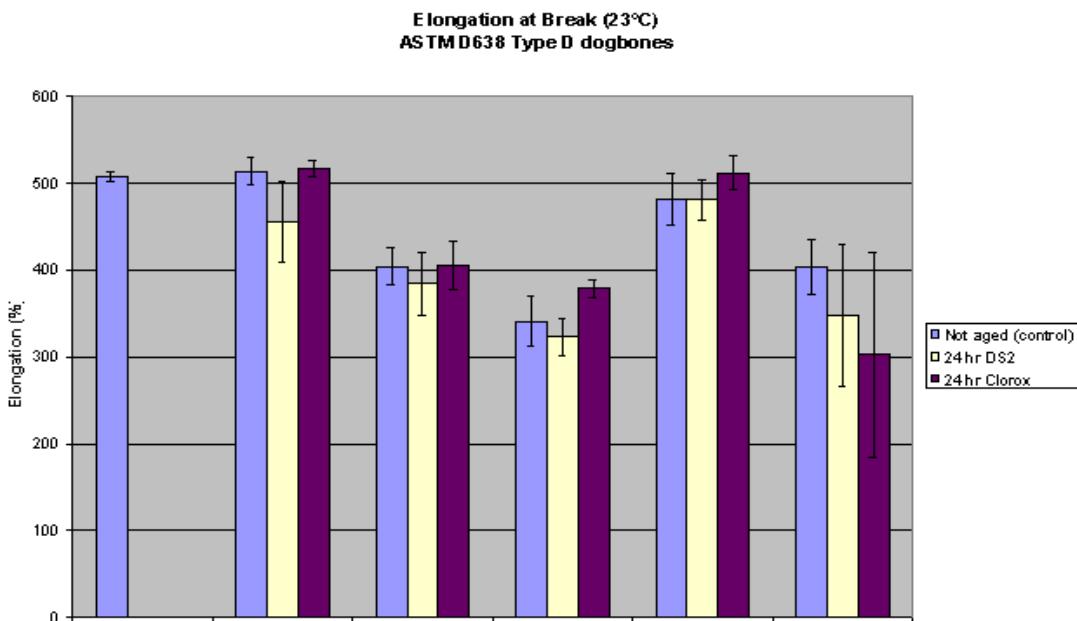


Figure 9. Effects on elongation using various decontamination solutions.

Currently FFF has the infrastructure and equipment in place to scale up for production. Current work is being done to improve efficiency, quality, and consistency of the entire process. FFF should be capable of producing enough material by the end of this year to demonstrate their capabilities. A prototype shelter will be constructed to further conduct physical, chemical and biological testing on this novel outer skin fabric.

Long-Term Solution

The long-term solution would involve a revolutionary new system such as a self-decontaminating barrier material incorporating catalytically reactive membranes. The U.S. Army is currently conducting a

technology watch to monitor and identify promising new breakthroughs in academia, industry, government agencies, and foreign military programs. Unfortunately, currently identified technology has to overcome technical barrier gaps such as the selectivity of the chemical reactions or stability of required enzymes in order to become a viable technology for collective protection.

CONCLUSION

Chemical and biological barrier materials are currently available for collective protection such as the M28 liner and the CBPSS. However, these materials inherently possess either cost or logistic barriers, which make fielding them undesirable unless a catastrophic effect is eminent. A lightweight, low cost, low packing volume, chemical and biological protective barrier material would make collective protection feasible for conventional shelter systems, therefore enhancing the safety of soldiers during unpredictable chemical and biological attacks.

Near-term, mid-term, and long-term solutions have been identified to allow incremental improvements over existing materials and further make collective protection a cost and logically effective option for every soldier on the battle field. These solutions are demonstrated and improved upon as new technologies or novel solutions are identified. The U.S Army in conjunction with the Joint Services are constantly seeking new ideas from academia, industry, government agencies, and foreign militaries, to overcome technical barriers which will allow the next quantum leap in collective protection.

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